Temperature-Controlled Cluster SIMS Depth Profiling in Polymeric Materials

Metrology to monitor the surface and in-depth molecular composition of polymeric materials is important for several applications spanning drug delivery and tissue engineering to microelectronics applications (e.g., photoresists, conducting polymers, and dielectric materials). This is because the performance characteristics of polymeric materials utilized in these applications are particularly sensitive to diffusion processes and compositional inhomogeneitities. With the development of cluster Secondary Ion Mass Spectrometry (SIMS), we have shown that we are now able to obtain spatially resolved surface and in-depth molecular information from several polymer systems and relate the sub-surface composition to the performance characteristics of real devices. However, this technology still has several limitations for polymeric depth profiling. The current work attempts to better understand the effect of temperature on depth profiling in polymeric materials.

C.M. Mahoney, A.J. Fahey, J.D. Batteas, and G. Gillen (Div. 837)

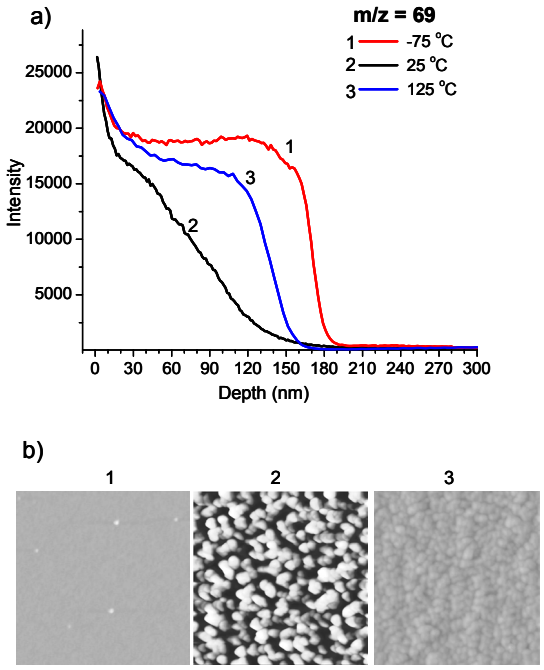
Cluster Secondary Ion Mass Spectrometry (SIMS) has been demonstrated to be a powerful tool to obtain spatially resolved surface and in-depth molecular information from polymer systems. However, this technology still has some limitations for polymeric depth profiling. For example, some polymers are more amenable to depth profiling with cluster SIMS than others (e.g., poly(lactic acid) performs better than poly(methylmethacrylate) (PMMA)), while still others experience extensive beam-induced degradation (e.g., polystyrene and polyethylene) resulting in total loss of signal. More research is required to acquire a better understanding of cluster SIMS of polymers and to determine what variables are important (e.g., temperature, sample rotation and presence of ambient gases) for optimum results. NIST is ideally suited to conduct this research as we have the appropriate instrumentation including three SIMS instruments equipped with variable temperature and rotatable stages in addition to several cluster primary ion sources including C_{60}^+, C_8^-, Bi_3^+, and SF_5^+.

The development of cluster SIMS for in-depth analysis of polymeric materials has potential long-term impact for quality control and product development in the biomedical/pharmaceutical, and microelectronics arenas.

It is expected that temperature will play a significant role in the success of polymeric depth profiles simply because there is a large variation in the physical properties of polymeric materials with temperature (e.g, density, modulus, thermal conductivity, heat capacity, etc.). Thus the corresponding sputter properties are expected to vary as well.

SIMS employing an SF_5^+ polyatomic primary ion source was used to depth profile through various polymeric biomaterials at a series of temperatures ranging from -125 °C to -150 °C.

Figure 1: (a) Positive secondary ion intensities of m/z = 69 plotted as a function of depth for a PMMA film (≈160 nm) on Si measured at: [1] -75 °C, [2] 25 °C, and [3] 125 °C. All depth profiles were acquired using dual beam depth profiling (Ar^+ analysis source and SF_5^+ sputter source). (b) Atomic Force Microscope (AFM) topography images of crater bottoms formed at different temperatures (1 µm x 1 µm area): [1] -75 °C, R_{rms} = ≈0.274 nm, [2] 25 °C, R_{rms} = ≈11.37 nm, and [3] 125 °C, R_{rms} = ≈1.00 nm.



The figure shows the resulting depth profiles of PMMA taken at different temperatures, where the curves in Figure 1a show the absolute secondary ion intensities of m/z = 69

($C_4H_5O^+$, a fragment ion characteristic of PMMA) plotted as a function of increasing depth (nm) at -75 ^oC (curve 1), 25 ^oC (curve 2) and 125 ^oC (curve 3). Note that this covers a temperature range above and well below the glass transition temperature (T_g) of PMMA (105 ^oC). Also illustrated in Figure 1b are the corresponding Atomic Force Microscopy (AFM) images of the crater bottoms (1 µm x 1 µm) taken at -75 ^oC (image 1), 25 ^oC (image 2) and 125 ^oC (image 3). As can be seen, the preferred temperature for depth profiling in PMMA using SF_5^+ is -75 ^oC, which results in constant secondary ion signals with increasing SF_5^+ dose (or depth), narrower interface widths, and very little sputter-induced topography formation as compared to other temperatures. Effects are also observed at 125 ^oC where there is an increase in the overall secondary ion stability, coupled with decreased sputter induced topography formation as compared to room temperature. These effects, however, are not as significant as was observed at low temperatures. It should also be noted that there was a large increase in the average sputter rate of PMMA at high temperatures. The effect of increasing sputter rate with temperature is thought to be a result of ion-induced depolymerization. Overall the worst depth profiles were obtained at room temperature as indicated by the rapid degradation in secondary ion signal, broadened interfacial regions, low substrate signals, and increased sputter-induced topography formation.

Future Plans: We intend to study the effects of sample rotation, presence of ambient gases, substrate composition, and other beam chemistries on polymeric depth profiles.

Publications:

Mahoney, C.M.; McDermott, M.K.; Patwardhan, D. ***"Characterization of Drug-Eluting Stent (DES) Materials with Cluster Secondary Ion Mass Spectrometry (SIMS)".*** Accepted, *Applied Surface Science*.

Mahoney, C.M.; Fahey, A.J.; Gillen, G.; Batteas, J.D. ***"Temperature-Controlled Depth Profiling in Polymeric Materials using Cluster Secondary Ion Mass Spectrometry (SIMS)".*** Accepted, *Applied Surface Science*.